Short communication

Effect of porosity on electrochemical properties of carbon materials as cathode for lithium-oxygen battery

Sang Bok Ma, Dong Joon Lee, Victor Roev, Dongmin Im*, Seok-Gwang Doo

Energy Storage Group, Energy Lab, Samsung Advanced Institute of Technology, Samsung Electronics, Giheung-gu, Yongin-si, Gyeonggi-do 446-712, Republic of Korea

HIGHLIGHTS

- Carbon aerogel shows much higher discharge capacity than activated carbons.
- Mesopores are more effective in the utilization of pore volume than micropores.
- Open pores help the oxygen supply even if they are micropores.

ARTICLE INFO

ABSTRACT

Porosity effect of carbon materials on the electrochemical performances as cathode materials in non-aqueous Li-oxygen cells has been investigated. A carbon aerogel material is chosen to represent meso-porosity and a couple of activated carbon materials are selected to represent microporosity. Carbon aerogel shows at least ten times higher discharge capacity (4155 mAh g^{-1}) than activated carbons. It is found that as much as 61% of pore volume of carbon aerogel is filled with discharge products (Li$_2$O$_2$) while less than 18% of pore volume is occupied with Li$_2$O$_2$ at the end of discharge in activated carbons, indicating that mesopore is more effective than micropore. In another experiments, the electrolyte impregnated electrode shows a capacitor-like discharge behavior, meaning it is necessary to have some open pore for the oxygen supply even though they are micropores.

1. Introduction

Much attention has been focused on the energy storage systems beyond Li-ion batteries. Li-air battery is one of the most promising candidates because it has a theoretical energy density over 3000 Wh kg^{-1} which is about 10 times greater than that of Li-ion battery [1–3]. Li-air battery uses oxygen from the air as active material, and thus may be charged and discharged by oxidation and reduction of oxygen in the cathode. The cathode reaction for the Li-air battery in non-aqueous electrolytes (especially in ether-based electrolytes) is widely assumed to be the Li$_2$O$_2$ formation as a discharge product by the reduction of oxygen during the first discharge [4]. The formed Li$_2$O$_2$ can be accumulated as a solid material in the pores of the cathode. The amount of Li$_2$O$_2$ is linearly proportional to the discharge capacity of Li-air battery. Therefore, the capacity of cathode is supposedly limited by its pore volume, with the assumption that the discharge product (Li$_2$O$_2$) fills that volume.

Carbon materials have been widely studied as cathode materials for Li-air batteries due to their high surface area, large pore volume, and high electrical conductivity. Pore of carbon materials can act not only as a channel for oxygen supply and electrolyte reservoir, but also as the storage space of the discharge product (Li$_2$O$_2$) for non-aqueous Li-air battery. Several studies have been reported on the pore characteristics and surface properties of carbon as cathode material [5–15]. Pore structure [6–10,12,13,15], oxygen channel [8,11], electrolyte wettability [14], loading level of electrode materials [5,11], binder amount [15], and electrolyte amount [5,8] were found to be important factors in improving the electrochemical performance of cathode. However, less effort has been devoted to systematically investigate the relationship between pore structures and electrochemical performances.

In this study, we have investigated carbon materials with the different pore size distribution including a couple of activated

* Corresponding author. Tel.: +82 31 2809601; fax: +82 31 2809359.
  E-mail address: dongmin.im@samsung.com (D. Im).

carbons with microporosity and a carbon aerogel with meso-porosity as cathode materials. We also have studied on the relationship between the electrolyte amount and the electrochemical performance of cathode.

2. Experimental

Two commercial activated carbon materials, YP-50F (Kuraray) and CEP21S (PTC), and a carbon aerogel (Enen) were used in this study. Their electrochemical performances were assessed with non-aqueous Li-air cells assembled in a dry room (dew point < −60 °C). The cell structure, which is similar to Lu et al.'s [16], is illustrated in Fig. 1. The cathode consisted of a mixture of carbon material and binder. Either carbon aerogel or activated carbon was mixed with 10 wt.% polyvinylidene fluoride (PVDF) dissolved in *N*-methylpyrrolidone as the binder. The slurry thus prepared was coated on an SGL 35BA gas diffusion layer and then dried in two steps (at 25 °C for 24 h, then at 120 °C for 2 h). Circular electrodes of 1.13 cm^2 area (dia. 12 mm) were cut for the cell assembly and each one contained around 4.5 mg of dried slurry (carbon + binder). Li foil with 500 μm thickness and same area to cathode was used as anode. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME). After assembling the Li-air cell as shown in Fig. 1, the cell was connected to an oxygen supply line and the oxygen pressure was maintained at 2 atm during the whole electrochemical test period. The Li-air cells were discharged from open circuit potential (OCP) to 2.0 V at a current of 0.1 or 0.2 mA by means of a potentiostat/galvanostat (1480 Multistat, Solartron Analytical).

A scanning electron microscopy (SEM, S-4500, Hitachi) was used to observe the morphology of the carbon aerogel and activated carbon powders. Porosity was investigated by N$_2$ adsorption desorption isotherms, which were collected on a Micromeritics Tristar system at liquid N$_2$ temperature. Prior to measurement, all samples were completely dried under vacuum at 100 °C for 24 h. The specific Brunauer–Emmett–Teller (BET) surface areas were calculated from the adsorption branches in the range of relative pressure $(p\ p_0^{-1}) = 0.05$–0.20. Pore size distribution curves were obtained from the adsorption branches by the Barrett–Joyner–Halenda (BJH) method.

3. Results and discussion

Fig. 2 shows SEM images of carbon aerogel and activated carbon materials (YP-50F and CEP21S). Large difference in morphology between carbon aerogel and activated carbon are recognized. The size of each carbon aerogel particle was in the range of 10–100 μm.
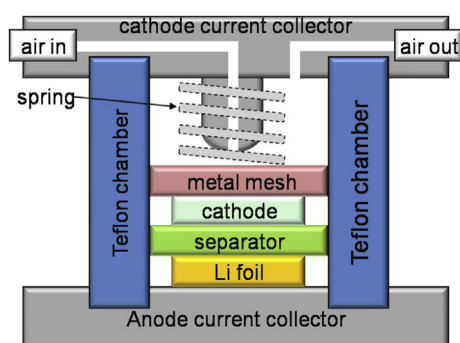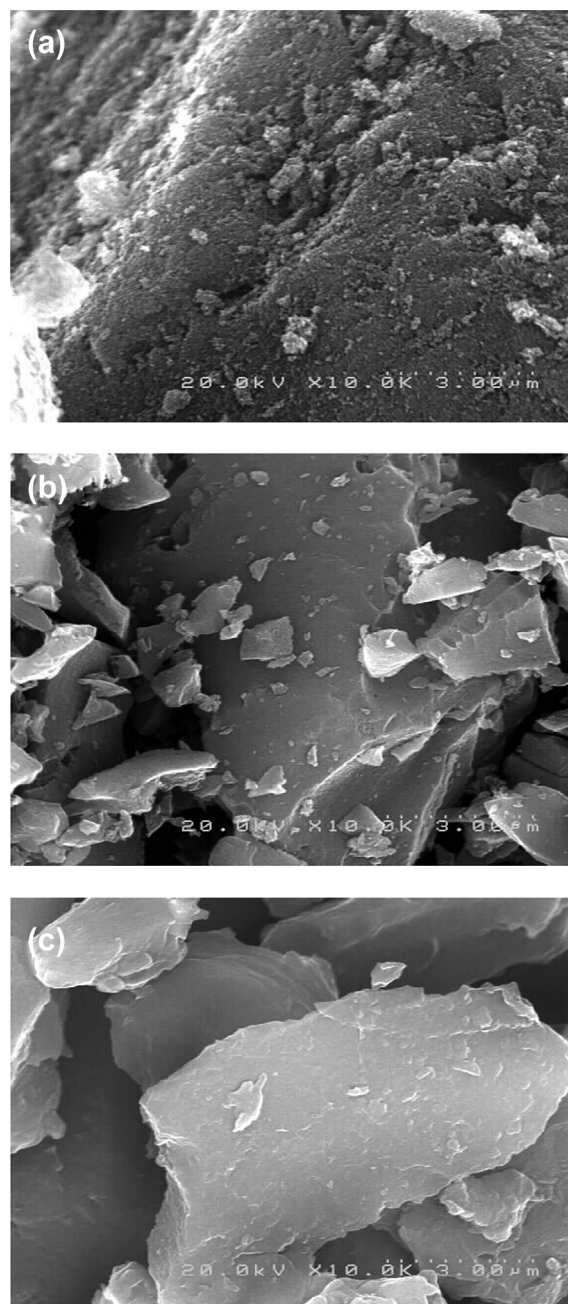

Fig. 2. SEM images of (a) carbon aerogel, (b) YP-50F, and (c) CEP21S activated carbons.

Activated carbon particles, however, have smaller sizes and more uniform size distribution between 5 and 20 μm as shown in Fig. 2b and c. Since the carbon aerogel has a much larger particle size than activated carbon, it can be inferred that the carbon aerogel might have a smaller surface area and larger interparticular pores. The surface of carbon aerogel surface appears rougher than that of activated carbon.

Pore characteristics of carbon aerogel and activated carbons have been measured with N$_2$ adsorption–desorption isotherms and are summarized in Table 1. Carbon aerogel exhibits a BET surface area of 688 m^2 g^{-1} and pore volume of 2.53 cm^3 g^{-1}. YP-50F and CEP21S show much larger surface area of 1908 and 1195 m^2 g^{-1} but smaller pore volume of 0.55 and 0.85 cm^3 g^{-1}, respectively. Due to the larger pore volume of carbon aerogel, it is anticipated that a larger amount of discharge products can be

Fig. 1. Illustration of a non-aqueous Li-air cell configuration for the investigation of the porosity effect of carbon materials.

Table 1
Pore characteristics of a carbon aerogel and activated carbons and their effect on electrochemical performance.

	Total pore volume $(cm^3 g^{-1})$[a]	BET surface area $(m^2 g^{-1})$[b]	Pore diameter (nm)[c]	Discharge capacity $(mAh\,g^{-1})$	Volume ratio of Li_2O_2 to pore in carbon[d]
Carbon aerogel	2.53	688	25–40	4155	0.61
Activated carbon (YP-50F)	0.55	1908	Less than 2	264	0.18
Activated carbon (CEP21S)	0.85	1195	Less than 2	124	0.05

[a] Total pore volumes measured at $p\,p_0^{-1} = 0.99$.
[b] BET surface areas calculated from the N_2 adsorption.
[c] Typical pore diameter range calculated by BJH method.
[d] Volume ratio of Li_2O_2 to pore = calculated volume of formed Li_2O_2 divided by total pore volume of carbon.

accommodated in the pores of carbon aerogel, resulting in a higher discharge capacity of the Li-air cell.

Fig. 3 shows that the N_2 sorption isotherms of carbon aerogel are of typical type IV behavior with hysteresis indicating characteristics of a mesoporous material [17]. On the other hand, type I behavior are identified in the isotherms of activated carbons (YP-50F and CEP21S), indicating microporosity [17]. The BJH pore size distribution curves (Fig. 4) obtained from the adsorption branch clearly show that carbon aerogel and activated carbon had thoroughly different pore characteristics. It has been revealed that the carbon aerogel has mesoporosity with a pore size range of 20–40 nm while both the activated carbons mainly comprise micropores with their diameter less than 2 nm. The well-defined step in the adsorption–desorption curves (Fig. 3) of carbon aerogel around the relative pressure ($p\,p_0^{-1}$) of 0.9 corresponds to the broad BJH pore size distribution between 20 and 40 nm. Since the typical pore size of carbon aerogel is about 10 times larger than those of activated carbons, oxygen supply and electrolyte accessibility to the reaction site through the pores of carbon aerogel can be much easier.

Fig. 5 and the inset of it show the first discharge profiles of the cathodes comprising carbon aerogel and activated carbons. The cells have been discharged from the open circuit potential to 2.0 V at a current of 0.1 mA (8.85×10^{-2} mA cm^{-1}). The profiles corresponding to carbon aerogel and activated carbon cathodes present typical discharge behavior of non-aqueous Li-air cells, indicating
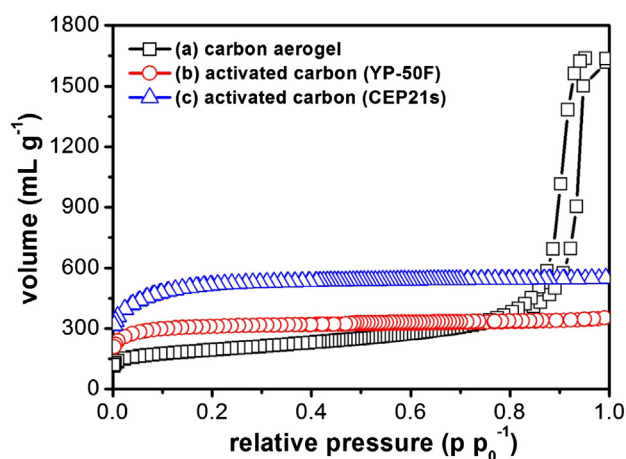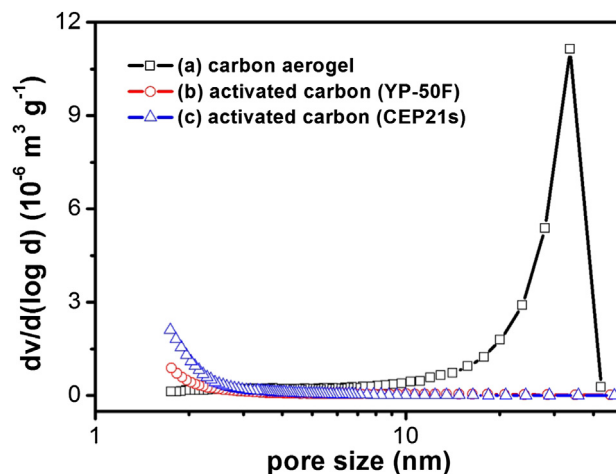

Fig. 4. BJH pore size distribution curves for (a) carbon aerogel, (b) YP-50F, and (c) CEP21S.

the oxygen reduction reaction involving the formation of Li_2O_2 [4]. Carbon aerogel exhibits a high specific capacity of 4155 mAh g^{-1} when calculated based on the weight of carbon. On the other hand, specific capacities of 264 and 124 mAh g^{-1} have been achieved with YP-50F and CEP21S activated carbons, respectively. The specific capacity of carbon aerogel is substantially higher than those of activated carbons even though the surface area of carbon aerogel (688 m^2 g^{-1}) is lower than those of activated carbons (1908 m^2 g^{-1} for YP-50F and 1195 m^2 g^{-1} for CEP21S). This is a strong evidence to confirm that large pore volume and mesoporosity are more important factors rather than surface area in determining the discharge capacity. The large pore volume in mesoporous carbon aerogel is believed to provide good electrolyte accessibility and enough space for the discharge products in non-aqueous Li-air cells.

Effect of porosity on electrochemical performance of carbon materials is also summarized in Table 1. The volume of Li_2O_2 formed at the end of discharge has been calculated from the total charge passed, assuming that the charge has been consumed solely by the following reaction:
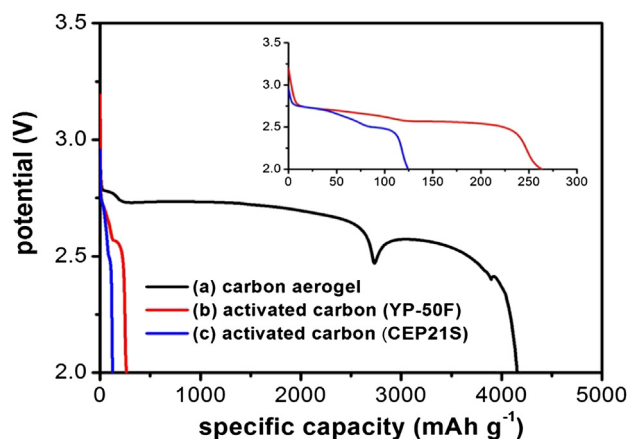
$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$$

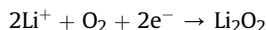**Fig. 3.** N_2 adsorption–desorption isotherms for (a) carbon aerogel, (b) YP-50F, and (c) CEP21S.

Fig. 5. First discharge curves for (a) carbon aerogel (b) YP-50F and (c) CEP21S at 0.1 mA from the open circuit potential to 2.0 V using 1 M LiTFSI in TEGDME.

where the density of Li_2O_2 is 2.31 g cm^{-3} and the molecular weight 45.88 g mol^{-1}.

Volume ratios of formed Li_2O_2 to pore in carbon have been calculated and are given in Table 1. In the case of carbon aerogel, Li_2O_2 generated by discharge process occupied 61% of pore volume. This means that 61% of pore has been utilized for storing discharge products. However, only 18% and 5% of the pore volume of carbon are occupied by Li_2O_2 for YP-50F and CEP21S activated carbons, respectively. The high utilization of pore volume of carbon aerogel might be mainly due to the mesoporous nature since it can provide high electrolyte accessibility and large oxygen channel. Conclusively, carbon aerogel shows 4.6 times higher pore volume, 10 times larger pore size, and 3.4 times better utilization of pore volume than activated carbons, resulting in 15.7 times higher discharge capacity.

Several studies on the relationship between the porosity of carbon and the discharge capacity have been reported. Mirzaeian et al. [6] proposed the relationship between the porosity of carbon aerogel and the discharge capacity in 1 M LiPF$_6$ in propylene carbonate. However, they used a large amount of manganese dioxide as catalyst in the cathode (weight ratio of carbon:manganese dioxide = 11:19) which might cause blocking the pore entrance and covering the surface of carbon. In addition, manganese dioxide and propylene carbonate could contribute to the discharge capacity of lithium-oxygen battery [18]. Yang et al. [12] also claimed that the primary factor governing the discharge capacity was the surface area and pore diameter of carbon by comparing a few carbon materials. However, they did not analyze the pore volume and its utilization quantitatively. In order to increase the accuracy of the relationship between the porosity of carbon and the discharge capacity, in our work, carbon materials without catalyst were used for cathode, TEGDME was employed as solvent instead of propylene carbonate due to its relative stability against superoxide attack [4], and a totally mesoporous carbon aerogel without micropores and totally microporous activated carbons without mesopores were chosen to unambiguously investigate the effect of pore characteristics such as surface area, pore size, pore volume, and the utilization of pore volume.

Fig. 6 shows the discharge profiles of YP-50F activated carbon and carbon aerogel electrodes before and after an electrolyte impregnation process, in which the electrode has been immersed in 1 M LiTFSI in TEGDME for 15 min under vacuum to thoroughly fill the pores of carbon with electrolyte. Discharge has been performed from the open circuit potential to 2.0 V at a current of 0.2 mA (1.77 × 10^{-1} mA cm^{-1}). The discharge curve of the YP-50F electrode

without electrolyte impregnation shows a potential plateau around 2.5 V, though it is very weak, indicating an oxygen reduction reaction forming Li_2O_2. However, the profile corresponding to the electrolyte impregnated cathode shows only a linear discharge curve without potential plateau indicating a capacitor-like behavior.

The carbon aerogel electrode shows a specific capacity as high as 500 mAh g^{-1} at 0.2 mA even in a fully soaked electrode as shown Fig. 6d. Tran et al. [8] announced that the behavior of double-layer capacitance rather than a battery behavior would be the dominating electrochemical phenomenon if the electrode is completely soaked with non-aqueous electrolyte. The electrochemical behavior of microporous carbon was consistent with literature. However, mesoporous carbon aerogel shows a long plateau (about 500 mAh g^{-1}) even after electrolyte impregnation, indicating the formation of Li_2O_2. This means that the mesoporosity can deliver larger capacity than the microporosity regardless of the electrolyte amount in the pore since the electrolyte reservoir helping the oxygen and lithium ion transport inside carbon aerogel should be larger than that of activated carbon even in the soaked electrodes.

The specific capacity of the electrolyte impregnated electrode has been reduced to the half of original one. This might be due to the blocking of oxygen supply channels by the electrolyte with completely filling the pores of carbon. It can be inferred that some pores need to be open to facilitate the oxygen supply inside the cathode. Therefore, in order to increase the utilization of the pores of carbon and enhance the formation of Li_2O_2 in carbon, not only the pore characteristics of carbon such as pore size and volume but also the existence of open pore is now considered an important factor.

Further works on optimizing the open pores for improved electrochemical performance and investigating a quantitative relation between the pore characteristics and electrochemical behavior are currently underway.

4. Conclusions

We have investigated the porosity effect of carbon materials on the electrochemical properties by employing a carbon aerogel with mesoporosity and a couple of activated carbons with microporosity as cathode materials for non-aqueous Li-air cells. Carbon aerogel showed a much higher discharge capacity of 4155 mAh g^{-1} than activated carbon materials (264 mAh g^{-1} for YP-50F and 124 mAh g^{-1} for CEP21S). In addition, the utilization of pore volume by Li_2O_2 was 61% for carbon aerogel while merely 18% and 5% of the pore volume of carbon were occupied by Li_2O_2 for YP-50F and CEP21S activated carbons. This indicates that mesopores are more effective than micropores to achieve higher discharge capacity and higher utilization of pores. The pore volume of carbon material was also found to be a more important factor than the surface area. It appears the pore volume plays a role in accommodating the discharge product in the cathode of Li-air battery. The electrode thoroughly impregnated with electrolyte showed a capacitor-like linear discharge profile without a potential plateau representing the formation of Li_2O_2 by an oxygen reduction reaction, revealing that the open pore was also significant for the oxygen supply to enhance the formation of Li_2O_2 in the pores of carbon.
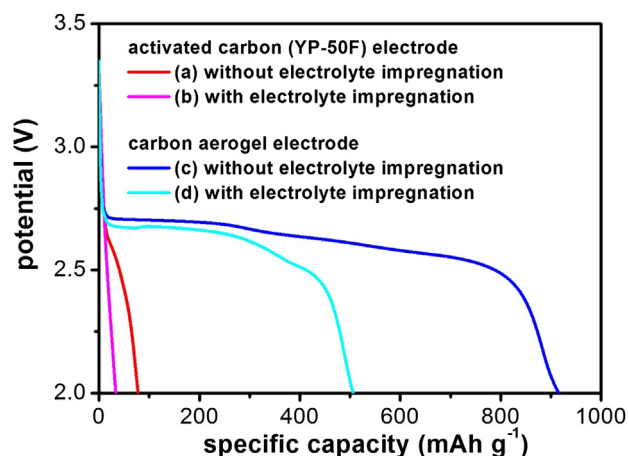

Fig. 6. First discharge profiles of activated carbon YP-50F electrodes (a) before and (b) after electrolyte impregnation, and carbon aerogel electrodes (c) before and (d) after electrolyte impregnation at 0.2 mA from the open circuit potential to 2.0 V using 1 M LiTFSI in TEGDME.

References

[1] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[2] A. Ogasawara, A. Debart, M. Holtzapfel, P. Novak, P.G. Bruce, J. Am. Chem. Soc. 129 (2006) 1390.
[3] A. Debart, J. Bao, G. Armstrong, P.G. Bruce, J. Power Sources 174 (2007) 1177.
[4] C.O. Laoire, S. Mukerjee, E.J. Plichta, M.A. Hendrickson, K.M. Abraham, J. Electrochem. Soc. 158 (2011) A302.
[5] J. Xiao, D. Wang, W. Xu, D. Wang, R.E. Williford, J. Liu, J.G. Zhang, J. Electrochem. Soc. 157 (2010) A487.
[6] M. Mirzaeian, P.J. Hall, Electrochim. Acta 54 (2009) 7444.

[7] M. Mirzaeian, P.J. Hall, J. Power Sources 195 (2010) 6817.
[8] C. Tran, X.Q. Yang, D. Qu, J. Power Sources 195 (2010) 2057.
[9] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, J. Power Sources 146 (2005) 766.
[10] Y. Wang, Electrochim. Acta 75 (2012) 239.
[11] G.Q. Zhang, J.P. Zheng, R. Liang, C. Zhang, B. Wang, M. Hendrickson, E.J. Plichtae, J. Electrochem. Soc. 157 (2010) A953.
[12] X.H. Yang, P. He, Y.Y. Xia, Electrochem. Commun. 11 (2009) 1127.
[13] X. Ren, S.S. Zhang, D.T. Tran, J. Read, J. Mater. Chem. 21 (2011) 10118.
[14] J. Read, J. Electrochem. Soc. 149 (2002) A1190.
[15] S.R. Younesi, S. Urbonaite, F. Bjorefors, K. Edstrom, J. Power Sources 196 (2011) 9835.
[16] Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, Y. Shao-Horn, Electrochem. Solid-State Lett. 13 (2010) A69.
[17] K. Kaneko, J. Membr. Sci. 96 (1994) 59.
[18] S.A. Freunberger, Y. Chen, Z. Peng, J.M. Griffin, L.J. Hardwick, F. Barde, P. Novak, P.G. Bruce, J. Am. Chem. Soc. 133 (2011) 8040.